EMI Shielding Properties of Carbon Nanofiber Filled Poly Vinlylidene Fluoride Coating Materials

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**Abstract:** The effectiveness of electromagnetic interference (EMI) shielding was measured for poly vinlylidene fluoride (PVDF) coating materials containing carbon nanofibers. When the thickness of carbon nanofibers filled PVDF coating materials varied from 25 to 100 μm, the electrical conductivity of coating materials was almost constant around 2.0 S/cm except for the case of 25 μm. Although the electrical conductivity should not change with the thickness of coating, the lower value with the thinner thickness could be related to the lack of uniformity at the lower thickness range. The specific surface area and electrical conductivity of filler were important factors for the shielding effectiveness (SE) of the coating materials. In order to apply carbon nanofibers as EMI shielding materials, large specific surface area and high electrical conductivity were desirable. The SE of the coating material showed a high value with the mild heat treatment at 1100 °C for 1 h and was proportional to the electrical conductivity of the coating materials.

**Keywords:** EMI, PVDF, carbon nanofibers, electrical conductivity, SE

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**Introduction**

Electronic equipments are all susceptible to malfunction as a result of electromagnetic interference (EMI). Therefore, an electrically conductive housing is needed to shield EMI produced from the electronic equipments. The shield should be highly conducting and thus metal is usually used. Metallic housing fabricated with steel, copper, aluminum, etc., were used by surrounding high EMI emitters for shielding. As commercial, military, and scientific electronic devices and communication instruments are used widely, there is an increased interest in shielding against electromagnetic radiation.

It is well known that high conducting materials like typical metals are well suited for many EMI shielding applications [1,2]. However, since shields fabricated with metals have shortcomings of heavy weight, corrosion, and physical rigidity, the electronics industry has resorted to metallized plating on plastics. Further efforts by the electronics industry to develop more dependable light weight materials for EMI shielding has led to electrically conductive component-filled plastic composites [3-6]. Carbon nanofibers are noble materials which can be produced by the decomposition of carbon containing gas over certain metal particles. Carbon nanofibers with high aspect ratio have advantages in both electrical conductivity and specific surface area. The high aspect ratio of fiber relative to other material forms enables the formation of a conductive pathway through the resin matrix at relatively low concentration.

The frequency permeability of composite materials has been studied theoretically and experimentally on a variety of materials [7,8]. In particular, it was deduced that, for composites made of a dispersion of carbon nanofibers particles in a matrix, the skin effect could drastically affect the measured permeability. When the coating layer thickness is not deep compared to the skin depth at a given frequency, the measured permeability is affected by the skin effect [9-11]. Electromagnetic radiation at high frequencies penetrates only the near surface region of an electrical conductor. The electric field of a plane wave penetrating a conductor drops exponentially with increasing depth into the conductor [12]. The depth at which the field drops to 1/e of the incident value is called the skin depth (δ) and it is given
by $\delta = (2\pi f \mu \sigma)^{1/2}$, where $f =$ frequency, $\mu =$ permeability, and $\sigma =$ bulk material conductivity. Hence, the skin depth decreases with increasing frequency, conductivity or permeability.

Conducting polymers are materials of increasing scientific and technical interest because of important high-tech applications. Variation of conductivity in polymer matrix by different treatments has been reported [13,14]. In this paper, the frequency permeability of composite materials containing conducting carbon nanofibers was investigated in the range of 500 MHz – 1.5 GHz frequency. Carbon nanofibers prepared by chemical vapor deposition of hydrocarbons with nickel-copper bimetallic catalysts were used as the conductive fillers. The objective of this study is to investigate the influence of coating thickness and heat treatment of the carbon nanofiber fillers on the EMI shielding effectiveness with carbon nanofiber filled PVDF coating materials.

**Experimental**

**Preparation of Carbon Nanofibers**

Carbon nanofibers with the diameters ranging 50 ~ 200 nm were prepared from the decomposition of propane, ethylene and acetylene gas over nickel-copper and pure nickel catalysts. The powder catalysts were prepared by co-precipitation of the metal carbonates from mixed nitrate solutions using ammonium bicarbonate. The precipitate was dried overnight at 110 °C, and then calcined in air for 4 h at 400 °C to convert the carbonate to mixed oxides, which were then reduced in hydrogen at 500 °C for 20 h. After the reduction, the reduced metals were cooled to room temperature under nitrogen purging. The metal was then passivated by the introduction of 2 vol.% of oxygen in nitrogen stream for 1 h. Preparation of carbon nanofiber were performed in a quartz reactor located in horizontal tube furnace.

**Preparation of Coating Materials**

The PVDF solutions were made by stirring the mixture containing 7 ~ 10 wt% of PVDF (Kynar® 731, ELF Atocchem) and 90 ~ 93 wt% of N-methyl-2-pyrrolidone (NMP, Micropure EG, ISD Technologies) at 60 °C for at least 30 min. The weight average molecular weight (Mw), number average molecular weight (Mn), and polydispersity (Mw/Mn) of PVDF were 3.26 × 10^5, 1.36 × 10^5, and 2.4 respectively. Carbon nanofibers or carbon blacks were crushed in a mechanical mixer. The crushed fillers (40 wt% of PVDF) were introduced into the PVDF solution, and the mixture was stirred at 600 rpm for 30 min by a mechanical stirrer and at 20000 ~ 40000 rpm for 3 min by a homogenizer continuously. The mixture obtained was coated into the size of 15 by 30 cm with the thickness of 180 ~ 900 μm using an applicator. The thickness of coating materials was measured by a blade gauge and reduced to 25 ~ 100 μm after drying.

**Characterization**

Due to the physical nature of carbon nanofiber fillers, conductivity measurement of by conventional methods proved to be an extremely difficult task. In order to determine the relative resistivity of the materials, a system consisted of ceramic tube fitted inside of stainless steel cylinder and two removable stainless steel pistons was built and tested. The electrical resistance between the contact points of the two stainless steel pistons was measured with a digital multimeter (Hioki Co., HI Tester 3220) while the carbon nanofiber sample in the chamber was kept under a constant pressure of 10000 psi. BET surface areas measurements were carried out by nitrogen adsorption at 196 °C using a surface area analyzer (Autosorb-1, Quantachrome). An automatic four-probe system (CMT-SR1000N, Chang Min Tech Co.) was used for measuring the electrical conductivity of coating materials. The measurement accuracy of the system was ± 0.5%. The SE of the coating materials was measured using a HP-8720C apparatus according to the method described in ASTM D 4935.

**Results and Discussion**

**Influence of Fillers and PVDF Concentration**

In order to compare the effectiveness of EMI shielding with different structure of carbon fillers, various carbon nanofibers were prepared from the decomposition of propane, ethylene and acetylene gas over nickel/copper 7:3 bimetallic (NC73) and pure nickel (N) catalysts. The carbon nanofibers obtained and a commercial carbon black (LG Chemical, Hi-black 41Y) were used as the fillers to fabricate PVDF composite coatings. Figure 1 represents SEM micrographs of the carbon nanofibers produced from ethylene/ NC73 systems and carbon nanofiber/PVDF coating materials. The morphology of carbon nanofibers was sensitive to the type of hydrocarbon gas. The carbon nanofibers prepared from propane consisted mostly of linear conformation and those from ethylene had mainly twisted conformation. The carbon nanofibers from acetylene had both twisted and helical conformation. It was reported that the carbon nanofibers with coiled or helical conformation were effective filler for EMI shielding [15]. Carbon nanofibers produced from the nickel-copper catalyst had relatively high specific surface areas compared with those from pure nickel catalyst.

Figure 2 represents the SE of carbon nanofibers and
Figure 1. SEM micrographs of carbon nanofibers prepared from decomposition of ethylene over Ni-Cu bimetallic catalysts and carbon nanofiber/PVDF coating materials.

Carbon black filled PVDF coating materials. In order to apply carbon nanofibers as an EMI shielding materials, high aspect ratio are desirable. As shown in Figure 2, since carbon nanofibers produced from the ethylene/NC73 system had higher SE than those from others, further experiments were performed with the carbon nanofibers from ethylene/NC73 system.

Figure 3 represents the SE of carbon nanofibers filled PVDF coating materials at various concentration of PVDF solution as a function of the frequency. The SE increased with the PVDF concentration rise up to 9 wt% and then decreased with the further increase of PVDF concentration. It was shown that the concentration of PVDF solution played an important role in improving the inhomogeneous behaviors of a coating material. Maximum SE value of carbon nanofibers filled PVDF coating materials occurred at around the 9 wt% concentration. The lack of SE with the high PVDF concentration of 10 wt% could be explained by the inhomogeneity of composite to form a good continuous network due to high viscosity of matrix and entanglement of carbon nanofibers.
Influence of Coating Thickness

Figure 4 represents the variation of the sheet resistance for the carbon nanofiber filled PVDF coating materials as a function of thickness. When the thickness of carbon nanofibers filled PVDF coating materials varied from 25 to 50 μm, the sheet resistance of coating materials decreased sharply from 283 to 105 Ω/sq and the electrical conductivity of coating materials increased from 1.34 to 1.91 S/cm. However, the sheet resistance reduced slowly and the electrical conductivity was almost constant around 2.0 S/cm with the further raise of the thickness. Although the electrical conductivity should not change with the thickness of coating since thickness term is cancelled out by normalization with thickness, the values were lower with the thickness below 50 μm. This behavior could be related to the lack of uniformity at the lower thickness range.

Figure 5 represents the shielding effectiveness of carbon nanofibers filled PVDF coating materials with various coating thickness. The dependence of coating thickness on SE was very similar to that on electrical conductivity of the coating materials. The SE increased dramatically with the increase of coating thickness up to 50 μm and then approached a certain value with the further raise of thickness. This phenomenon denotes that a critical thickness of coating materials exists around 50 μm and may be related to the skin effect, which can occur with coating thickness around the skin depth. When the coating layer thickness is less than the skin depth, the measured permeability is affected by the skin effect.

Effect of Heat Treatment Temperature and Time

Table 1 represents the physical properties of carbon nanofibers and their PVDF coating materials as a function of heat treatment temperature and time for the carbon nanofiber fillers. Specific surface area of the carbon nanofiber fillers decreased with the increase of the heat treatment temperature and time. The relative changes in the internal and external surface areas are presented in Table 1. The decrease in the surface area could be explained by the removal of the open, internal porosity during the heat treatment. Surface rearrangement and loss of porosity in the carbon particle at temperatures above 1000 °C lead to a rapid decrease in

![Figure 4. Sheet resistance of carbon nanofiber filled PVDF coating materials with different thickness and 9% PVDF concentration.](image)

![Figure 5. Shielding effectiveness of carbon nanofibers filled PVDF coating materials with different thickness and 9% PVDF concentration.](image)

<table>
<thead>
<tr>
<th>Nano fibers from</th>
<th>Heat treatment of filler (h/1100 °C)</th>
<th>Specific surface area (m²/g) (external/internal)</th>
<th>Electrical conductivity of filler (S/cm)</th>
<th>Electrical conductivity of coating material (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₃H₆/NC73</td>
<td>Raw material</td>
<td>202 (161/41)</td>
<td>5.6</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td>1/1100</td>
<td>83 (64/19)</td>
<td>14.4</td>
<td>2.41</td>
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<td></td>
<td>12/1100</td>
<td>61 (59/2)</td>
<td>18.4</td>
<td>2.32</td>
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<tr>
<td></td>
<td>1/2700</td>
<td>54 (54/0)</td>
<td>22.4</td>
<td>1.97</td>
</tr>
</tbody>
</table>
surface area [16]. With the increase of heat treatment temperature and time, the electrical conductivity of filler increased, while that of carbon nanofibers filled PVDF coating material showed a high value with the mild heat treatment at 1100 °C for 1 h and then decreased with the further increase of heat treatment temperature and time. The specific surface area and electrical conductivity of carbon nanofibers were important properties for EMI shielding. As EMI filler, large specific surface area of carbon nanofibers is desirable. It was reported that filler's specific surface area was a more important factor than the filler's conductivity [17]. As the result, it was known that the filler's specific surface area has influenced the electrical conductivity of coating material. Figure 6 represents the SE of carbon nanofiber filled PVDF coating materials as a function of heat treatment temperature and time. The SE of coating materials showed at a similar fashion with the electrical conductivity of coating materials as the carbon nanofibers were heat-treated.

Conclusions

Carbon nanofibers were dispersed as conductive fillers in a PVDF matrix and the influence of coating thickness and heat treatment of carbon-nanofiber filler on the SE of resulting composites were investigated. When the thickness of carbon nanofibers filled PVDF coating materials varied from 25 to 100 μm, the electrical conductivity of coating materials was almost constant around 2.0 S/cm except for the case of 25 μm. Although the electrical conductivity should not change with the thickness of coating, the lower value with the thinner thickness could be related to the lack of uniformity at the lower thickness range. The SE of coating materials showed a maximum at the mild heat treatment and was proportional to the electrical conductivity of coating materials. It was concluded that both the filler's specific surface area and electrical conductivity have influenced the electrical conductivity of coating materials.

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References